

WO 99/36039

PCT/FR98/02831

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COMPOSITION FOR THE OXIDATION DYEING OF KERATIN FIBRES,
CONTAINING A LACCASE, AND DYEING PROCESS USING THIS
COMPOSITION

5 The invention relates to a composition for
the oxidation dyeing of keratin fibres, and in
particular of human keratin fibres such as the hair,
comprising, in a medium which is suitable for dyeing,
at least one heterocyclic oxidation dye and at least
10 one laccase-type enzyme, as well as to the dyeing
process using this composition.

It is known practice to dye keratin fibres,
and in particular human hair, with dye compositions
containing one or more oxidation dye precursors, in
15 particular ortho- or para-phenylenediamines, ortho- or
para-aminophenols, and heterocyclic bases, which are
generally known as oxidation bases. These oxidation
dyes (oxidation bases) are colourless or weakly
coloured compounds which, when combined with oxidizing
20 products, can give rise to coloured compounds and dyes
by a process of oxidative condensation.

It is also known that the shades obtained
with these oxidation bases can be varied by combining
them with couplers or coloration modifiers, the latter
25 being chosen in particular from aromatic meta-diamines,
meta-aminophenols, meta-diphenols and certain
heterocyclic compounds.

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patent applications FR-A-2 112 549, FR-A-2 694 018,
EP-A-0 504 005, WO 95/07988, WO 95/33836, WO 95/33837,
WO 96/00290, WO 97/19998 and WO 97/19999, to dye
keratin fibres with compositions comprising at least
5 one oxidation dye, or at least one melanin precursor,
in combination with laccase-type enzymes, the said
compositions being placed in contact with atmospheric
oxygen. Although these dye formulations are used under
conditions which do not result in the degradation of
10 keratin fibres comparable to that generated by dyes
used in the presence of hydrogen peroxide, they lead to
colorations that are still insufficient both in terms
of the homogeneity of the colour distributed along the
fibre (unison) and in terms of the chromaticity
15 (luminosity) and dyeing power.

The Applicant has now discovered that it is
possible to obtain novel dyes that are capable of
giving more intense colorations without generating any
significant degradation of keratin fibres, and that are
20 relatively unselective and stand up well to the various
attacking factors to which the fibres may be subjected,
by combining at least one suitably selected
heterocyclic oxidation dye (oxidation base and/or
coupler) and at least one laccase-type enzyme.

25 This discovery forms the basis of the present
invention.

A first subject of the invention is thus a
ready-to-use composition for the oxidation dyeing of

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keratin fibres, and in particular of human keratin fibres such as the hair, characterized in that it comprises, in a medium which is suitable for dyeing,

- at least one oxidation dye chosen from heterocyclic oxidation bases and heterocyclic couplers, and
- at least one laccase-type enzyme,

the said composition being free of heterocyclic coupler chosen from indole, indoline, monocyclic pyridine and phenazine compounds and free of heterocyclic oxidation base chosen from 4,5-diamino-6-hydroxypyrimidine and 3,4-diaminohydroxypyrazole.

The ready-to-use dye composition in accordance with the invention leads to intense, chromatic colorations. The colorations obtained with the ready-to-use dye composition in accordance with the invention moreover show little selectivity and excellent properties of resistance both with respect to atmospheric agents such as light and bad weather and with respect to perspiration and the various treatments to which hair may be subjected (washing, permanent-waving).

A subject of the invention is also a process for the oxidation dyeing of keratin fibres using this ready-to-use dye composition.

The laccase(s) used in the ready-to-use dye composition in accordance with the invention can be chosen in particular from laccases of plant origin, of animal origin, of fungal origin (yeasts, moulds or

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fungi) or of bacterial origin, it being possible for the organisms of origin to be monocellular or multicellular. The laccase(s) used in the ready-to-use dye composition in accordance with the invention can
 5 also be obtained by biotechnology.

Among the laccases of plant origin which can be used according to the invention, mention may be made of the laccases produced by plants which carry out chlorophyll synthesis, such as those mentioned in
 10 patent application FR-A-2 694 018.

Mention may be made in particular of the laccases present in extracts of Anacardiaceae plants such as, for example, extracts of *Magnifera indica*, of *Schinus molle* or of *Pleiogynium timoriense*; in extracts
 15 of Podocarpaceae plants, of *Rosmarinus off.*, of *Solanum tuberosum*, of *Iris sp.*, of *Coffea sp.*, of *Daucus carota*, of *Vinca minor*, of *Persea americana*, of *Catharanthus roseus*, of *Musa sp.*, of *Malus pumila*, of *Gingko biloba*, of *Monotropa hypopithys* (Indian pipe),
 20 of *Aesculus sp.*, of *Acer pseudoplatanus*, of *Prunus persica* and of *Pistacia palaestina*.

Among the laccases of fungal origin, optionally obtained by biotechnology, which can be used according to the invention, mention may be made of the
 25 laccase(s) obtained from *Polyporus versicolor*, from *Rhizoctonia praticola* and from *Rhus vernicifera* as described, for example, in patent applications FR-A-2 112 549 and EP-A-504 005; the laccases described in

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such as 2,4,5,6-tetraaminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine, and the addition salts thereof with an acid and pyrazolo-pyrimidine derivatives such as pyrazolo[1,5-a]pyrimidine-3,7-diamine,

- 5 2-methylpyrazolo[1,5-a]pyrimidine-3,7-diamine, 2,5-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine, pyrazolo[1,5-a]pyrimidine-3,5-diamine, 2,7-dimethylpyrazolo[1,5-a]pyrimidine-3,5-diamine, 3-aminopyrazolo[1,5-a]pyrimidin-7-ol, 3-amino-5-
- 10 methylpyrazolo[1,5-a]pyrimidin-7-ol, 3-aminopyrazolo[1,5-a]pyrimidin-5-ol, 2-(3-aminopyrazolo[1,5-a]pyrimidin-7-ylamino)ethanol, 3-amino-7- β -hydroxyethylamino-5-methylpyrazolo-[1,5-a]pyrimidine, 2-(7-aminopyrazolo[1,5-a]pyrimidin-
- 15 3-ylamino)ethanol, 2-[(3-aminopyrazolo[1,5-a]pyrimidin-7-yl)-(2-hydroxyethyl)amino]ethanol, 2-[(7-amino-pyrazolo[1,5-a]pyrimidin-3-yl)-(2-hydroxyethyl)amino]-ethanol, 5,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine, 2,6-dimethylpyrazolo[1,5-a]pyrimidine-
- 20 3,7-diamine and 2,5,N7,N7-tetramethylpyrazolo-[1,5-a]pyrimidine-3,7-diamine, and the addition salts thereof and the tautomeric forms thereof, when a tautomeric equilibrium exists.

Among the pyrazole derivatives which may be

25 mentioned more particularly are the compounds described in patents or patent applications DE 3 843 892, DE 4 133 957, DE 4 234 886, WO 94/08969, WO 94/08970, DE 4 234 887, FR 2 733 749, FR 2 735 685, such as

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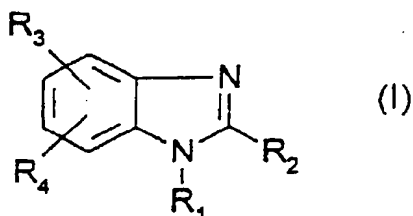
4,5-diaminopyrazole, 4,5-diamino-1-methylpyrazole,
 1-benzyl-4,5-diaminopyrazole, 3,4-diaminopyrazole,
 1-benzyl-4,5-diamino-3-methylpyrazole, 4-amino-1,3-
 dimethyl-5-hydrazinopyrazole, 4,5-diamino-3-methyl-1-
 5 phenylpyrazole, 4,5-diamino-1-tert-butyl-3-
 methylpyrazole, 4,5-diamino-3-tert-butyl-1-methyl-
 pyrazole, 4,5-diamino-1-ethyl-3-methylpyrazole,
 4,5-diamino-1-ethyl-3-(4'-methoxyphenyl)pyrazole,
 4,5-diamino-1-ethyl-3-hydroxymethylpyrazole,
 10 4,5-diamino-3-hydroxymethyl-1-methylpyrazole,
 4,5-diamino-3-hydroxymethyl-1-isopropylpyrazole and
 4,5-diamino-3-methyl-1-isopropylpyrazole, and the
 addition salts thereof with an acid.

Among the heterocyclic couplers which can be
 15 used in the ready-to-use dye composition in accordance
 with the invention, mention may be made in particular
 of benzimidazole derivatives, benzomorpholine
 derivatives, sesamol derivatives, pyrazoloazole
 derivatives, pyrroloazole derivatives, imidazoloazole
 20 derivatives, pyrazolopyrimidine derivatives,
 pyrazoline-3,5-dione derivatives, pyrrolo-
 [3,2-d]oxazoline derivatives, pyrazolo[3,4-d]thiazole
 derivatives, thiazoloazole S-oxide derivatives and
 thiazoloazole S,S-dioxide derivatives, and the addition
 25 salts thereof with an acid.

Among the benzimidazole derivatives which can
 be used as heterocyclic couplers in the dye composition
 in accordance with the invention, mention may be made

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more particularly of the compounds of formula (I) below, and the addition salts thereof with an acid:



in which:

- 5 R_1 represents a hydrogen atom or a C_1 - C_4 alkyl radical,
 R_2 represents a hydrogen atom or a C_1 - C_4 alkyl or phenyl radical,
 R_3 represents a hydroxyl, amino or methoxy radical,
 R_4 represents a hydrogen atom or a hydroxyl, methoxy or
 10 C_1 - C_4 alkyl radical;
 with the proviso that:
- when R_3 denotes an amino radical, then it occupies position 4,
 - when R_3 occupies position 4, then R_4 occupies position
 15 7,
 - when R_3 occupies position 5, then R_4 occupies position
 6.

Among the benzimidazole derivatives of formula (I) above which may be mentioned more
 20 particularly are 4-hydroxybenzimidazole,
 4-aminobenzimidazole, 4-hydroxy-7-methylbenzimidazole,
 4-hydroxy-2-methylbenzimidazole, 1-butyl-4-hydroxy-
 benzimidazole, 4-amino-2-methylbenzimidazole,
 5,6-dihydroxybenzimidazole, 5-hydroxy-6-methoxy-

EP-A-244 160, EP-A-578 248, GB 1 458 377, US 3 227 554,
 US 3 419 391, US 3 061 432, US 4 500 630, US 3 725 067,
 US 3 926 631, UA 5 457 210, JP 84/99437, JP 83/42045,
 JP 84/162548, JP 84/171956, JP 85/33552, JP 85/43659,
 5 JP 85/172982, JP 85/190779 as well as in the following
 publications: Chem. Ber. 32, 797 (1899), Chem. Ber. 89,
 2550, (1956), J. Chem. Soc. Perkin trans 1, 2047,
 (1977), J. Prakt. Chem., 320, 533, (1978); the
 teachings of which form an integral part of the present
 10 patent application.

Pyrazoloazole derivatives which may be
 mentioned most particularly are:

- 2-methylpyrazolo[1,5-b]-1,2,4-triazole,
- 2-ethylpyrazolo[1,5-b]-1,2,4-triazole,
- 15 - 2-isopropylpyrazolo[1,5-b]-1,2,4-triazole,
- 2-phenylpyrazolo[1,5-b]-1,2,4-triazole,
- 2,6-dimethylpyrazolo[1,5-b]-1,2,4-triazole,
- 7-chloro-2,6-dimethylpyrazolo[1,5-b]-1,2,4-triazole,
- 3,6-dimethylpyrazolo[3,2-c]-1,2,4-triazole,
- 20 - 6-phenyl-3-methylthiopyrazolo[3,2-c]-1,2,4-triazole,
- 6-aminopyrazolo[1,5-a]benzimidazole,

and the addition salts thereof with an acid.

Among the pyrroloazole derivatives which can
 be used as heterocyclic couplers in the ready-to-use
 25 dye composition in accordance with the invention,
 mention may be made more particularly of the compounds
 described in the following patent applications and
 patents: US 5 256 526, EP-A-557 851, EP-A-578 248,

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EP-A-518 238, EP-A-456 226, EP-A-488 909, EP-A-488 248,
and in the following publications:

- D.R. Liljegren Ber. 1964, 3436;
- E.J. Browne, J.C.S., 1962, 5149;
- 5 - P. Magnus, J.A.C.S., 1990, 112, 2465;
- P. Magnus, J.A.C.S., 1987, 109, 2711;
- Angew. Chem. 1960, 72, 956;
- and Rec. Trav. Chim. 1961, 80, 1075; the teachings of
which form an integral part of the present patent
10 application.

Pyrroloazole derivatives which may be
mentioned most particularly are:

- 5-cyano-4-ethoxycarbonyl-8-méthylpyrrolo[1,2-b]-
1,2,4-triazole,
- 15 - 5-cyano-8-methyl-4-phenylpyrrolo[1,2-b]-
1,2,4-triazole,
- 7-amido-6-ethoxycarbonylpyrrolo[1,2-a]benzimidazole,
and the addition salts thereof with an acid.

Among the imidazoloazole derivatives which
20 can be used as heterocyclic couplers in the ready-to-
use dye composition in accordance with the invention,
mention may be made more particularly of the compounds
described in the following patent applications and
patents: US 5 441 863; JP 62-279 337; JP 06-236 011 and
25 JP 07-092 632, the teachings of which form an integral
part of the present patent application.

Imidazoloazole derivatives which may be
mentioned most particularly are:

- 7,8-dicyanoimidazolo[3,2-a]imidazole,
 - 7,8-dicyano-4-methylimidazolo[3,2-a]imidazole,
- and the addition salts thereof with an acid.

Among the pyrazolopyrimidine derivatives

5 which can be used as heterocyclic couplers in the ready-to-use dye composition in accordance with the invention, mention may be made more particularly of the compounds described in the following patent application: EP-A-304 001, the teaching of which forms

10 an integral part of the present patent application.

Pyrazolopyrimidine derivatives which may be mentioned most particularly are:

- pyrazolo[1,5-a]pyrimidin-7-one,
- 2,5-dimethylpyrazolo[1,5-a]pyrimidin-7-one,
- 15 - 2-methyl-6-ethoxycarbonylpyrazolo[1,5-a]pyrimidin-7-one,
- 2-methyl-5-methoxymethylpyrazolo[1,5-a]pyrimidin-7-one,
- 2-tert-butyl-5-trifluoromethylpyrazolo[1,5-
- 20 a]pyrimidin-7-one,
- 2,7-dimethylpyrazolo[1,5-a]pyrimidin-5-one, and the addition salts thereof with an acid.

Among the pyrazoline-3,5-dione derivatives which can be used as heterocyclic couplers in the

25 ready-to-use dye composition in accordance with the invention, mention may be made more particularly of the compounds described in the following patent

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fibres are rinsed, optionally washed with shampoo, rinsed again and dried.

The time required to develop the coloration on the keratin fibres is generally between 3 minutes
5 and 60 minutes and even more specifically between 5 minutes and 40 minutes.

According to one specific embodiment of the invention, the process includes a preliminary step consisting in separately storing, on the one hand, a
10 composition (A) comprising, in a medium which is suitable for dyeing, at least one oxidation dye chosen from the heterocyclic oxidation bases and heterocyclic couplers as defined above, and, on the other hand, a composition (B) comprising, in a medium which is
15 suitable for dyeing, at least one laccase-type enzyme, and then in mixing them together at the time of use, after which this mixture is applied to the keratin fibres.

Another subject of the invention is a multi-
20 compartment dyeing device or "kit" or any other multi-compartment packaging system, a first compartment of which contains composition (A) as defined above and a second compartment of which contains composition (B) as defined above. These devices may be equipped with a
25 means for applying the desired mixture to the hair, such as the devices described in patent FR-2 586 913 in the name of the Applicant.

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The example which follows is intended to illustrate the invention without thereby limiting its scope.

DYEING EXAMPLE

- 5 The following ready-to-use dye compositions were prepared (contents in grams):

COMPOSITION	1	2
2,4,5,6-Tetraaminopyrimidine sulphate (heterocyclic oxidation base)	0.65	-
para-Phenylenediamine (benzenic oxidation base)	-	0.20
Resorcinol (benzenic coupler) /	0.30	-
2-Methoxy-4,5-methylenedioxyaniline monohydrochloride (heterocyclic coupler)	-	0.37
Laccase obtained from Rhus vernicifera at 180 units/mg, sold by the company Sigma	1.8	1.8
Common dye support (*)	(*)	(*)
Demineralized water qs	100 g	100 g

(*): Common dye support:

- Ethanol 20.0 g
- 10 - (C8-C10)alkylpolyglucoside as an aqueous solution containing 60% active material (A.M.), sold under the name Oramix CG110[®] by the company Seppic 4.8 g A.M.
- 15 - Agent for pH q.s. pH = 6.5

Each of the ready-to-use dye compositions described above was applied to locks of natural grey hair containing 90% white hairs, for 40 minutes at a temperature of 30°C. The hair was then rinsed, washed
5 with a standard shampoo and then dried.

The hair was dyed in the shades given in the Table below:

EXAMPLE	Shade obtained
1	Coppery mahogany light blond
2	light blond

In the dye compositions described above, the
10 laccase from *Rhus vernicifera* at 180 units/mg, sold by the company Sigma, can be replaced with 1.0 g of laccase from *Pyricularia oryzae* at 100 units/mg, sold by the company ICN.

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